

Bench-scale Kinetics Study of Mercury Reactions in FGD Liquors

Paper #47

David W. DeBerry, Ph.D. and Gary M. Blythe, URS Corporation, 9400 Amberglenn Blvd., Austin, TX 78729

Sara Pletcher, National Energy Technology Laboratory, U.S. Department of Energy, 3610 Collins Ferry Road, Morgantown, West Virginia 26507

Richard Rhudy, EPRI, 3412 Hillview Avenue, Palo Alto, CA 94304

ABSTRACT

Oxidation of gas phase elemental mercury followed by absorption of the oxidized product with a wet flue gas desulfurization (FGD) absorber is a promising method for mercury removal from power plant flue gases. However, in at least some FGD systems reduction of oxidized mercury back to elemental mercury occurs and the mercury is re-emitted. The objective of the project is to determine the mechanisms and kinetics of the aqueous reactions of mercury absorbed by wet FGD systems and to use this information to develop a kinetics model which predict mercury reactions in wet FGD systems over a wide range of chemical conditions. The model will be used to determine optimum wet FGD design and operating conditions to maximize mercury capture in wet FGD systems. This project is being co-funded by DOE-NETL and EPRI and is currently scheduled to be completed at the end of calendar year 2006. This presents and discusses an overview of results to date.

INTRODUCTION

Oxidation of gas phase elemental mercury followed by absorption of the oxidized product with a wet flue gas desulfurization (FGD) absorber is a promising method for mercury removal from power plant flue gases. However, in at least some FGD systems reduction of oxidized mercury back to elemental mercury occurs and the mercury is re-emitted. There is ample evidence that mercury re-emission reactions (apparently driven by SO₂-derived "sulfite" species in the liquid phase) are limited by kinetics rather than equilibrium. Fundamental laboratory studies of the kinetics of mercury reactions in the aqueous phase are currently being conducted as part of this project.^{1,2,3} A review of the literature produced an initial series of chemical reactions between oxidized mercury and sulfite ion that could lead to re-emissions, and additional pathways have been identified as described here. Experimental methods have been developed to identify reaction intermediate species and to track their changes in concentration as the reactions proceed. Separate but complementary methods of following the rate of evolution of mercury in the gas phase, and loss of mercury from the liquid phase have also been developed and applied.

Major effects of chloro-mercuric sulfite complexes on re-emissions reaction mechanisms and kinetics over a wide range of FGD operating conditions have been found. The data collected have been used to develop a kinetics model. The model will be verified in tests conducted with a bench-scale wet FGD system, where both gas-phase and liquid-phase mercury concentrations will be measured to determine if the model accurately predicts the tendency for mercury re-emissions and the phase in which mercury is found in the FGD byproducts. Modifications to the bench-scale wet FGD apparatus are underway, and a preliminary test matrix has been developed. The validated model will be run over a wide range of potential wet FGD design and operating conditions to determine conditions that maximize mercury capture, minimize mercury re-emissions, and/or predict conditions where the captured mercury will exit the system in the byproduct solids rather than in blow down liquor or vice-versa.

EXPERIMENTAL

This project has focused on obtaining kinetic data under conditions common to wet FGD systems in such a way that effects of individual composition and physical variables can be determined. SO₂-derived species such as the various forms of "sulfite" are important since this is the main source of reductant for converting oxidized mercury to elemental mercury. Kinetic measurements have been done for solutions containing chloride and thiosulfate, both of which may form strong complexes with Hg⁺². Another important variable is pH, which affects both the distribution of sulfite species and the kinetics of many reactions. Most of the testing has been conducted with sulfite and chloride added as sodium salts, to avoid potential interferences from complexes that calcium and magnesium ions can form with these species. However, the effects of other major species in FGD liquors, such as magnesium, calcium, sulfate and NO_x-derived species, will also be determined, as will the possible catalytic effects of particulate matter. In addition to chemical species effects, the effects of temperature and ionic strength on kinetics are being measured. Most of the work has been done in the normal FGD temperature range (50-55°C), but activation energies are measured or estimated as necessary for modeling.

Prior research has shown that key Hg-sulfite species have intense absorption peaks in the UV range and thus can be monitored as a function of time by taking periodic spectral measurements.⁴ Current instrumentation allows rapid gathering of complete UV/Vis spectra (up to 50 spectra per second) or monitoring light absorbance at up to six wavelengths simultaneously as desired. This greatly enhances the ability to obtain both pathway information (by following multiple peaks in the spectra) and kinetics data for construction of a meaningful model.

The experimental apparatus consists of a spectrophotometric cell housed in a special cell holder with fiber optic hookups to a UV/Vis light source and a CCD spectrometer. The spectrometer and cell holder are computer controlled, enabling precise control and rapid sampling. The spectrophotometric system includes a high-resolution CCD miniature fiber optic spectrometer. The light source combines deuterium and tungsten halogen light sources into a single optical path. The cuvette (measurement cell) holder is a fiber optic temperature-controlled unit which provides precise temperature control ($\pm 0.02^\circ\text{C}$) of the 1-cm cuvette reaction vessel, built-in magnetic stirring, a dry gas purge to limit condensation or exclude oxygen from the cuvette, and optical slits for control of the illuminated volume.

Since the reactions studied thus far have been fairly slow, a simple but effective manual mixing method has been used to obtain kinetics data. Typically 2.00 mL of solution containing mercuric perchlorate and a pH buffer is placed in the spectrophotometric cell and temperature equilibrated in the cuvette holder. Continuous acquisition of spectra is initiated, typically taking a complete spectrum every five seconds. About 10 spectra are obtained for background subtraction purposes, then a small amount of sulfite solution is injected into the stirred spectrophotometric cell to start the reaction (typically 20-50 microliter [μL] using a microliter pipetter). This addition results in the abrupt appearance of a peak in the 230-235 nm region due to formation of mercuric disulfite, the predominant aqueous complex formed between mercury ion and sulfite ion. The decay of this peak is then monitored by continuing to take spectra for up to several hours.

In unraveling complex chemical kinetics, it is important to measure as many of the participating chemical species as possible, including both reactants and products. Therefore, tests have been done which measure the evolution of Hg^0 from solution both by making gas phase Hg measurements on the outlet gas and measuring the amount of total mercury remaining in a continuously sparged solution. The test apparatus for this procedure consists of a reaction vessel (sparger) charged with an aqueous solution containing a buffer for pH control and other chemical species, such as chloride, as desired. A gas stream containing nitrogen, SO_2 , and presaturated with water is passed through this solution at a constant rate, typically 1.0 L/min. The SO_2 concentration in the gas and pH are chosen to give the desired SO_2 (sulfite species) concentration in the liquid.

The sparged reaction vessel is submerged in a water bath temperature controlled to $\pm 0.1^\circ\text{C}$. To start the reaction a solution containing mercuric ion is injected into the sparged solution via a hypodermic syringe and septum. Elemental mercury sparged from the reaction vessel is measured using a UV gas cell spectrophotometer and a 254 nm mercury lamp (an atomic absorption analyzer) as a function of time using computer controlled data acquisition. Alternatively, for slow reaction rate conditions the liquid phase is periodically sampled and the preserved solutions analyzed for mercury by FIMS (cold vapor atomic absorption).

KINETICS MEASUREMENT RESULTS

Results are presented here starting with the simpler systems (mercuric ions and sulfite) and the spectrophotometric measurement procedures and proceeding to more complicated systems with addition of chloride and other chemical species. We then show results of the experimental methods based on measuring the gas phase evolution of mercury from sparged solutions, or periodic analysis for liquid phase mercury.

"Raw" spectrophotometric results are shown in terms of absorbance (proportional to concentration of absorbing species) as a function of time. In all cases a 1.00 cm path length cell was used and for the simplest case (starting with only oxidized mercury and sulfite). The primary species absorbing near 230 nm is mercuric disulfite [$\text{Hg}(\text{SO}_3)_2^{-2}$] which has an absorptivity of $3.0 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$.⁴ For this case an absorbance of 1.0 corresponds to approximately $3.3 \times 10^{-5} \text{ M}$

$\text{Hg}(\text{SO}_3)_2^{-2}$. A decrease in absorbance thus corresponds to the disappearance of this species to form elemental mercury, as given by the following overall reaction:

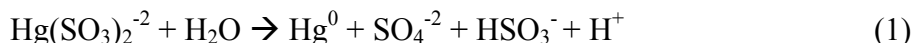
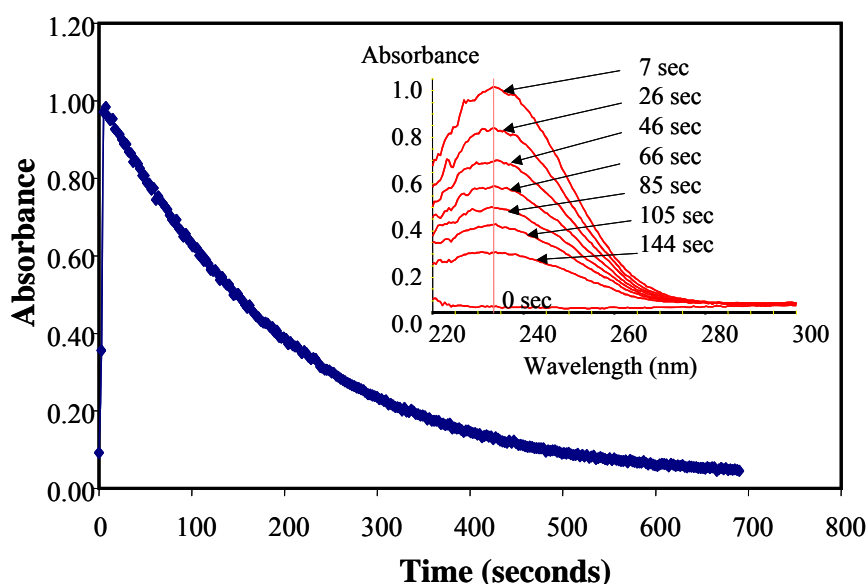


Figure 1 shows an example of absorbance (at 233 nm) vs. time results for the formation and decay of $\text{Hg}(\text{SO}_3)_2^{-2}$ on mixing 40 micromolar (μM) total Hg^{+2} with 0.23 mM total sulfite at pH 3.0 and 45°C. The inset in the figure shows the type of spectra used to generate the plot in Figure 1, although the inset data were obtained under slightly different conditions of 0.18 mM total sulfite. The wavelength used for the absorbance curve was selected by inspection of the peaks for each run. The peaks occasionally varied over a range of several nm during the run.

Figure 1. Experimental Absorbance and Spectra Data for Mercury Disulfite

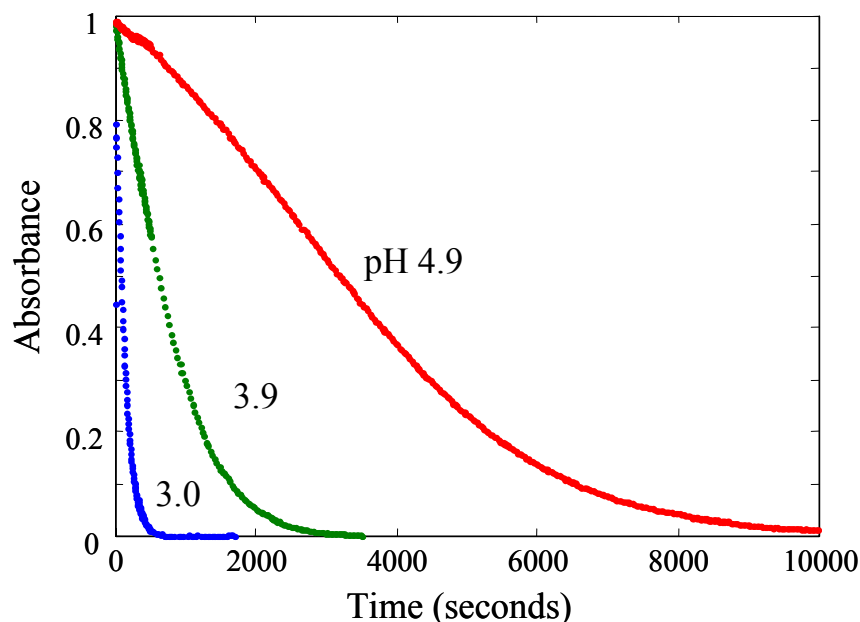


The effect of pH on the absorbance profiles is shown in Figure 2 for solutions without chloride at 55 °C and initially containing 1.0 mM sulfite and 40 μM Hg^{+2} . As shown, the rate of mercuric complex decomposition slows considerably in going from pH 3.0 to pH 3.9, and even more when the pH is adjusted to 4.9. The lower pH values in the figure represent the pH a droplet might achieve as it falls through an FGD absorber rather than a bulk reaction tank slurry pH, which would be in the range of pH 5 to 7.

In the pH 4.9 case, the shape of the absorbance - time curve starts to deviate significantly from what one would expect from a simple first order reaction, which should produce more of an asymptotic decay similar to the plot in Figure 1. However, for the purposes of comparing results from run to run to quantify variable effects, an "observed" rate constant, k_{obs} , has been calculated for each assuming a simple first order reaction. This is obtained from a least squares fit of the experimental data using the equation:

$$\ln A_t = \ln A_0 - k_{\text{obs}} t \quad (2)$$

Figure 2. Effect of pH on Rate Curves (no chloride; 55 °C; 1.0 mM sulfite; 40 μM Hg^{+2})



A good fit to this equation is obtained only for the more "ideal" results, but even for conditions where the fit was poorer it is useful to use this value for comparison purposes. As an example, a plot of $\log k_{\text{obs}}$ versus pH has a slope of about -0.76, suggesting that the rate is close to being inversely proportional to hydrogen ion concentration in the absence of chloride and other complexing agents.

The effect of sulfite on the reaction profiles is shown in Figure 3 for solutions without chloride, at pH 3.9 and 55 °C and initially containing 40 μM Hg^{+2} . The lowest sulfite concentration gives the fastest reaction rate, followed by the intermediate sulfite concentration, with the highest sulfite showing both a very slow decomposition rate and considerable departure from ideal first order behavior. A log-log plot for k_{obs} and sulfite concentration gives a reaction order of -1.18, suggesting that the reduction rate is inversely proportional to sulfite concentration at these conditions.

Runs have been done from 45 °C to 55 °C at pH 3.0, in the absence of chloride, with initially 1.0 mM sulfite and 40 μM Hg^{+2} . The results for an Arrhenius plot using k_{obs} gives an activation energy of 39.2 kcal/gmole, close to the literature value of 39.7 kcal/gmole.⁴ This is a high activation energy, which tends to make the reduction of Hg^{+2} by sulfite quite sensitive to temperature.

Addition of low concentrations of chloride produces quite different time profiles. Figure 4 shows the effects of starting the reaction with 10 mM chloride. The lower initial absorbance indicates that the apparent initial concentration of $\text{Hg}(\text{SO}_3)_2^{-2}$ is lowered (or more likely the UV absorbing species is changed, see below) when chloride is present, and there is a major difference in the rate of disappearance of the absorbing species. The value of k_{obs} for the run without chloride is about 20 times that of the run with chloride.

Figure 3. Effect of Sulfite on Rate Curves (no chloride; 55 °C; pH 3.9; 40 μM Hg^{+2})

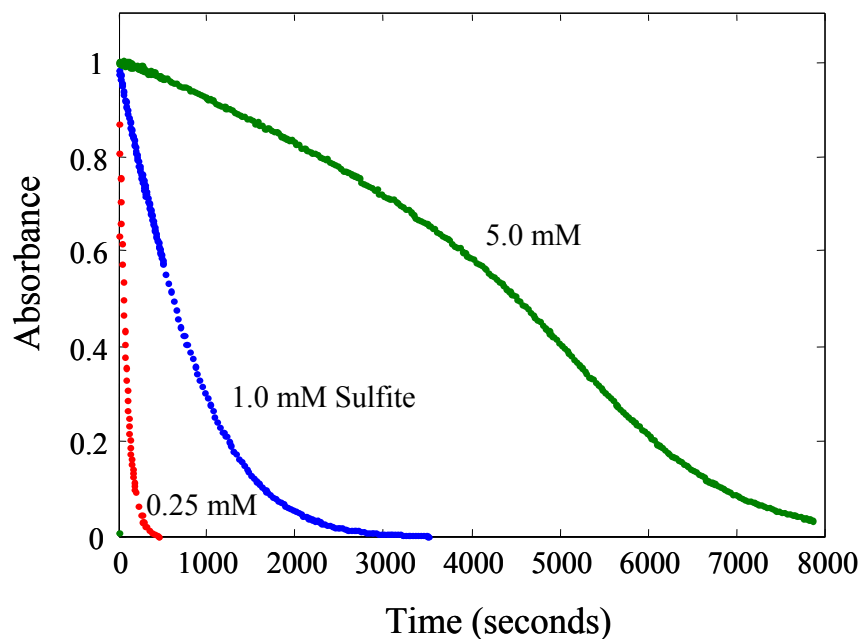
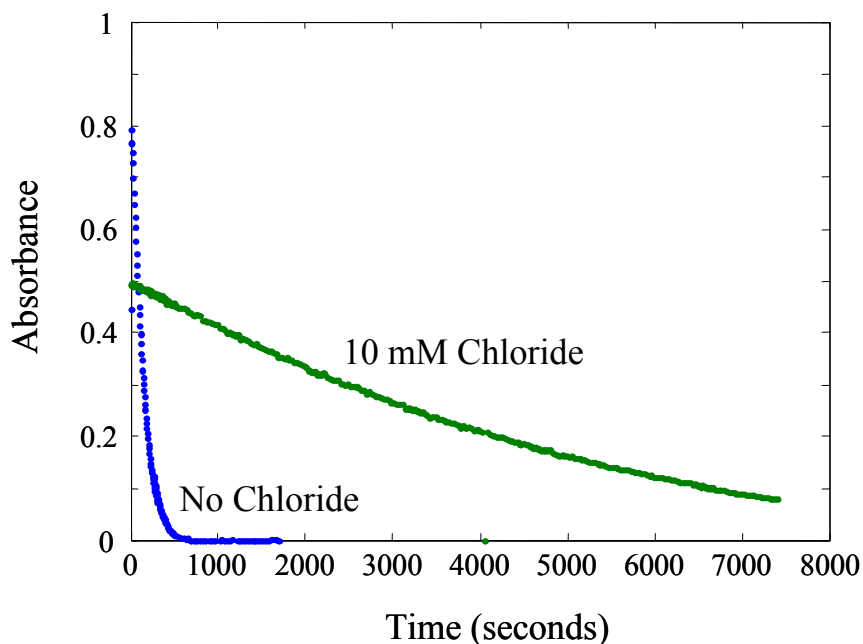


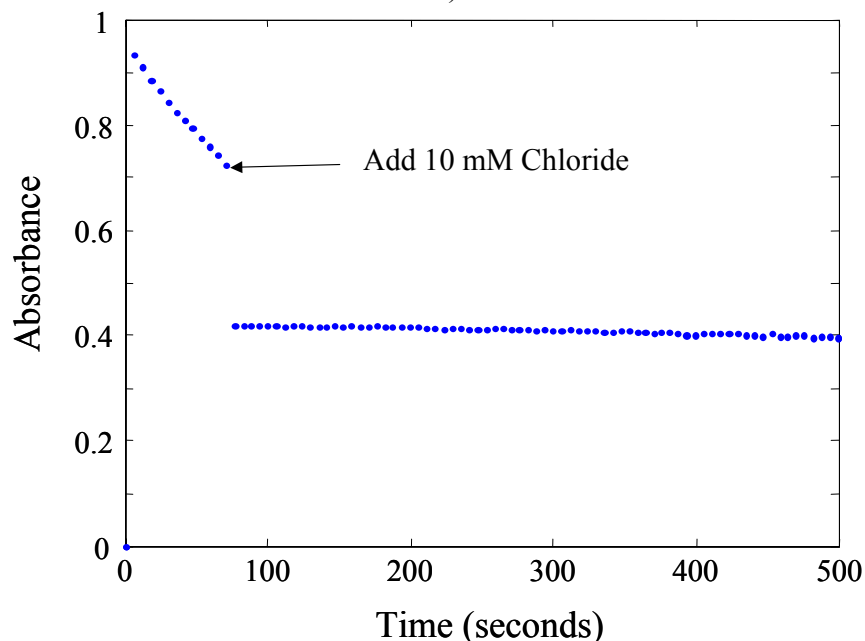
Figure 4. Effect of Chloride on Rate Curve (pH 3.0, 55 °C, 1.0 mM sulfite, 40 μM Hg^{+2})



The drastic change in rate can also be observed with a different order of reagent mixing. Figure 5 shows a run that was started without any chloride present. Chloride was injected about 70 seconds into the run, resulting in the sharp drop in absorbance noted in the figure, and the change to the much slower disappearance noted at later times. The run was continued for over 7500

seconds, and the k_{obs} calculated from data obtained after chloride injection was within 25% of the value found when the run was done with chloride initially present.

Figure 5. Effect of Adding Chloride After Start of Run (1.0 mM sulfite, 55 °C, 40 μM Hg^{+2} , pH 3.0)

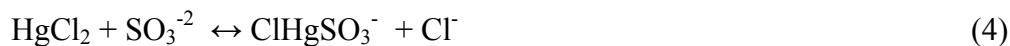


Further examination of the complete spectra from this run showed that there was a small but definite shift of about 4-5 nm in the spectral peak wavelength when the chloride was added. This shift was essentially completed during the 5 seconds that elapsed between spectrum acquisition. This same difference in spectral peak wavelength is noted in the individual runs done with and without chloride addition. The peak values occur at approximately 232 nm with chloride and 237 nm without chloride. This behavior suggested the formation of a different complex than the mercuric disulfite $[\text{Hg}(\text{SO}_3)_2^{-2}]$ complex formed in the absence of chloride.

Inspection of analytical chemistry literature showed that mixed chloride-sulfite mercuric complexes have been suspected in analytical methods for SO_2 that use tetrachloromercurate as an absorbent. Dasgupta and DeCesare assigned a spectral peak similar to the one we observed to the complex ClHgSO_3^- , but did not investigate it in detail.⁵ We have been able to "titrate" sulfite into a solution of mercuric ion with a low concentration of chloride present. This was done at a low temperature of 10 °C to minimize mercury reduction. The absorbance increases rapidly as sulfite is added up to about 0.04 mM sulfite, which is equal to the original concentration of mercuric ion, then changes much more slowly with further increases in sulfite concentration.

This is consistent with the formation of a 1:1 complex between a chlorinated Hg^{+2} species and SO_3^{-2} , rather than the 2:1 complex between Hg^{+2} and SO_3^{-2} to form mercuric disulfite. Even more complicated behavior is seen as the concentration of chloride is increased. Considerable effort has been required to unravel the interplay between kinetics and equilibria of formation of multiple complexes of Hg^{+2} with Cl^- and SO_3^{-2} . For example, the kinetics may be affected by the

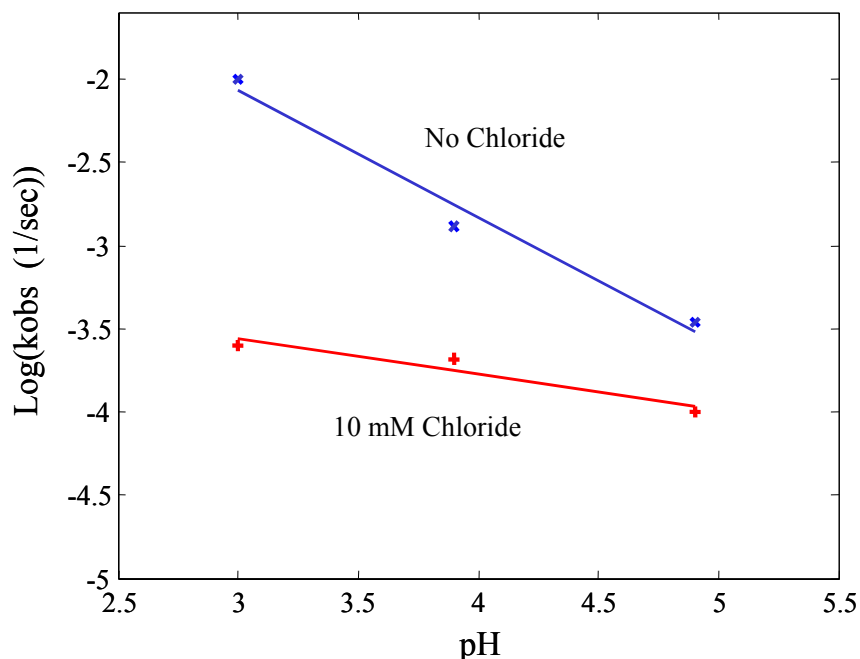
formation of other mercury complexes containing both chloride and sulfite, along with their decomposition reactions as shown below:



According to our current model, the $\text{Cl}_2\text{HgSO}_3^{-2}$ does not decompose (or decomposes at a negligible rate).

Chloride also has a substantial effect on the pH dependence of the reaction. The initial absorbance changes with pH when chloride is present, but the slopes of the curves are close to being the same. This is quantified by a plot of $\log(k_{\text{obs}})$ versus pH, which is relatively flat for the 10 mM chloride case (a slope of only -0.21), as shown in Figure 6.

Figure 6. pH Dependence of k_{obs} with and without 0.01 M Chloride (55°C, 1.0 mM sulfite, 40 μM Hg^{+2})



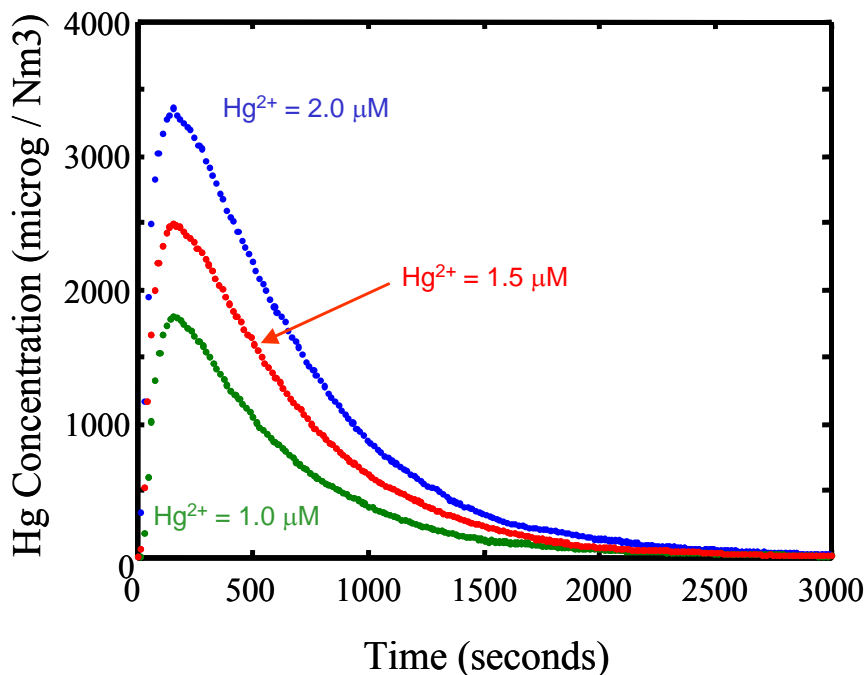
Although much progress has been made, it is difficult to interpret and determine all of the necessary information for modeling based on spectrophotometric results alone. Therefore, other approaches such as the “mercury stripping” tests and tests with simultaneous redox potential, spectrophotometric, and pH monitoring were used to supplement spectrophotometric results. The elemental mercury stripping tests are described below.

The stripping rate method measures the amount of gas phase elemental mercury produced by the reactions as a function of time. In one mode the apparatus can measure gas phase mercury

concentrations directly in a continuous manner, without having to use gold amalgamation in semi-continuous measurements. The gas phase Hg^0 is measured directly in a 17.5 cm flow tube using a 254 nm mercury lamp source and photomultiplier detector. The absorptivity of gas phase Hg^0 was taken as $4.1 \times 10^6 \text{ L}/(\text{gmole cm})$.⁶ This approach provides a direct measurement and much shorter time between measurements which is good for fast reaction conditions, but is subject to long term drift and is difficult to apply at low mercury concentrations. Therefore we use liquid phase mercury measurements for very slow reaction conditions.

Typical results obtained with this equipment are shown in Figure 7 for three different levels of Hg^{+2} injected at $t = 0$. These runs were done at 55 °C with 124 ppm SO_2 , balance N_2 in the gas passing through the absorber. This corresponds with a sulfite level of 1.3 mM and pH of 3.1.

Figure 7. Hg^0 Stripping Kinetics Results for Addition of 1.0, 1.5, and 2.0 μM Hg^{+2} to Solution Containing 1.3 mM Sulfite at pH 3.1, with 124 ppm SO_2 in Gas Phase at 55 °C

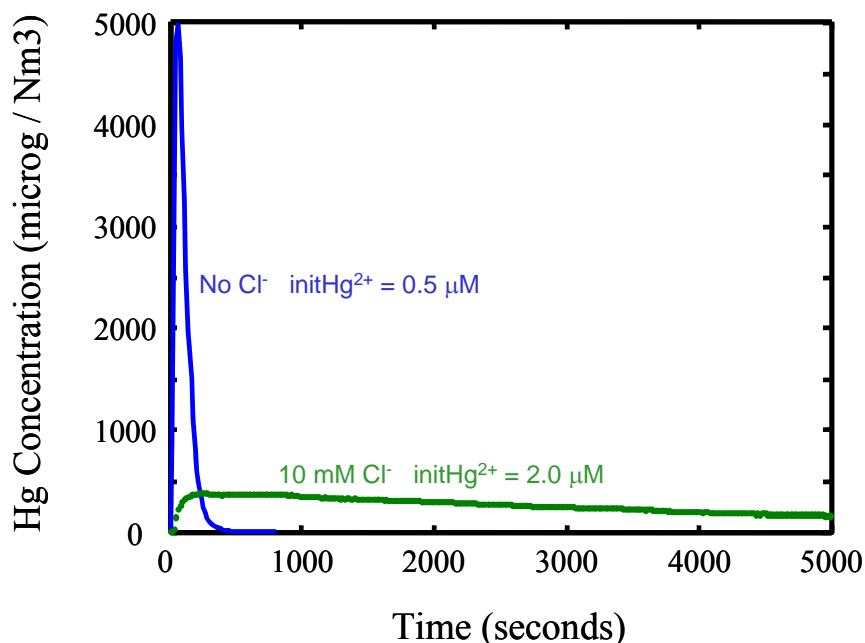


As shown in Figure 7, elemental mercury starts to evolve at once, reaches a peak, and then shows a decline similar in shape to the spectrophotometric decay curves of the mercuric sulfite complex that have been shown previously. Values of the "observed" rate constant, k_{obs} , were calculated from the slope of the natural log of absorbance versus time in the absorbance decay region of the figure. For these three runs the k_{obs} was essentially the same, $2.0 \pm 0.15 \times 10^{-3} \text{ sec}^{-1}$, as would be expected for a reaction that is first order in dissolved Hg^{+2} overall. This is also in very good agreement with the k_{obs} calculated from the corresponding spectrophotometric experiment, $3 \times 10^{-3} \text{ sec}^{-1}$ (which would be expected to be somewhat higher since it was done at lower sulfite concentration, 1.0 mM vs. 1.3 mM).

The effect of adding 10 mM chloride on re-emission kinetics is shown in Figure 8. As expected from the spectrophotometric work, both the amount of Hg emitted and the rate of emissions is

lowered drastically. The average k_{obs} from three stripping runs is $1.7 \pm 0.7 \times 10^{-4} \text{ sec}^{-1}$ and is again in good agreement with the spectrophotometric value of about $2 \times 10^{-4} \text{ sec}^{-1}$.

Figure 8. Re-emission Kinetics Results with and without 10 mM Chloride at 55 °C

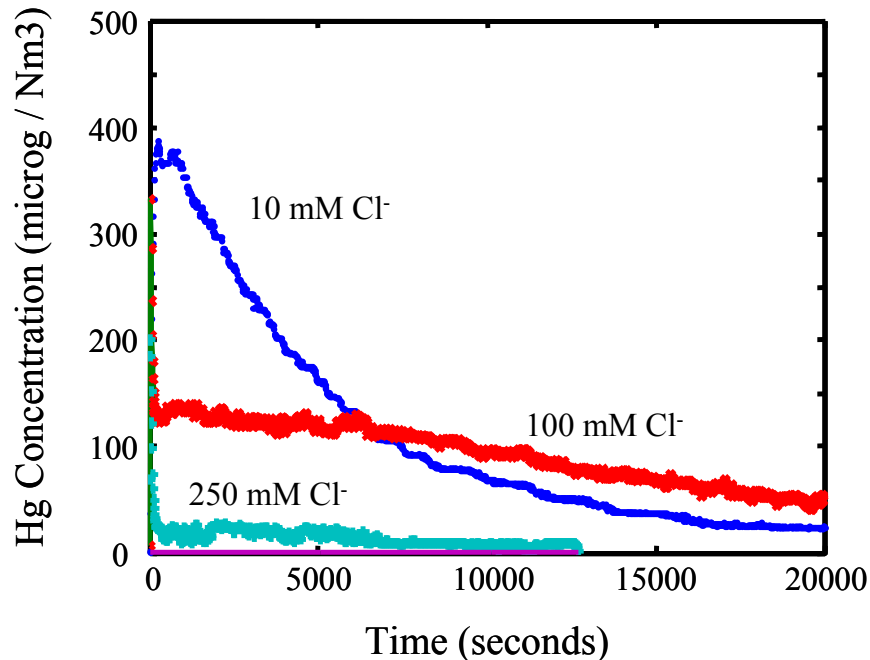


A comparison of Hg emission kinetics for runs with 10 mM, 100 mM, and 250 mM chloride is shown in Figure 9. The 10 mM (~350 ppm) chloride run started with an injection of $2.0 \mu\text{M}$ Hg^{+2} . The 100 (~3500 ppm) and 250 mM (~8900 ppm) chloride runs used ten times the initial amount of mercury ($20 \mu\text{M}$ Hg^{+2}), to produce measurable vapor phase Hg^0 concentrations.

Again, the data in this figure show that each increasing level of chloride substantially decreases the overall amount and rate of evolution of Hg^0 from the solution. There is typically a "spike" of Hg^0 released at the start of the run. This may be associated with a spike in absorbance seen at the start of many of the high chloride spectrophotometric runs but more work is needed to establish a relationship.

The sorbent liquids from the initial set of stripping kinetics runs (done with gas phase mercury analysis) were analyzed for mercury after each run by cold vapor atomic absorption. Over 99.5% of the mercury was stripped out of the solution in the 0 and 10 mM chloride cases. For the 100 mM chloride case only 37 % of the added mercury was stripped and for the 250 mM chloride case less than 3 % was stripped after a total run duration of more than 50 hours. To put these chloride concentrations into the perspective of typical FGD liquor chloride concentrations, 10 mM (~350 ppm) would represent a very low FGD chloride ion concentration, while 100 mM (~3500 ppm) would represent a mid-range value for an FGD system with a moderate chloride purge rate. The highest value of 250 mM (~8900 ppm) is not atypically high for FGD systems with a lower chloride purge rate (e.g., systems that produce wallboard-grade gypsum), which can range up to 10 times that chloride concentration.

Figure 9. Stripping Kinetics Results with 10 mM, 100 mM and 250 mM Chloride at 55 °C



We have briefly looked at the effects of thiosulfate ion (present in inhibited oxidation FGD liquors) on mercury reduction using the gas phase stripping kinetics method. The mercuric-thiosulfate complexes are strong and have high UV absorbance, complicating spectrophotometric measurement even at low thiosulfate concentrations. Results of a stripping kinetics using 1.0 mM thiosulfate added to a 100 mM chloride solution are compared in Figure 10 to those obtained without thiosulfate but also with 100 mM chloride; both were spiked with 20 μM Hg^{+2} . Note that 1.0 mM of thiosulfate (~110 ppm) is a relatively low concentration compared to typical values in inhibited oxidation FGD liquors, where values of 10 to 30 mM are common.

As can be seen, the initial sharp Hg^0 emission peak is very similar in the two cases. In the case without thiosulfate there follows a period of slowly declining evolution of Hg^0 . In the thiosulfate case, however, the Hg^0 evolution essentially goes to zero after the initial spike. Analysis of the thiosulfate solution for mercury concentration indicated that less than 10% of the original mercury had been stripped after over 21 hours. Less than 0.1% of the added mercury could be accounted for in the gas phase for this run. Thus, it appears that even low concentrations of thiosulfate inhibit Hg^0 evolution under these conditions, probably due to formation of mercuric-thiosulfate complexes which are stable and which block the more rapid reduction pathways involving chloromercuric sulfite complexes.

Another interesting example of effects of a strong complexing agent is shown in a run done with only 80 μM iodide (~10 ppm), which is compared to results with 80 μM of chloride (~ 3 ppm) under the same pH 3.0, 1.0 mM sulfite, and 55 °C conditions in Figure 11.

The response with 80 μM chloride is similar to and about as fast as without chloride, indicating that chloride cannot compete very well with sulfite in complexing (and reducing) mercuric ion at

Figure 10. Effect of Adding 1.0 mM Thiosulfate to a 100 mM Chloride Solution on Hg^0 Stripping Kinetics

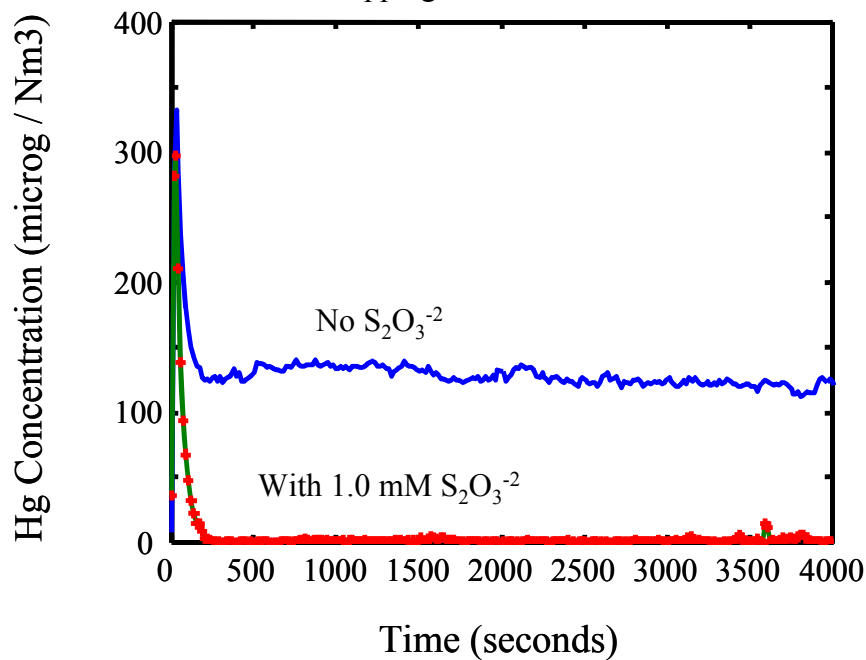
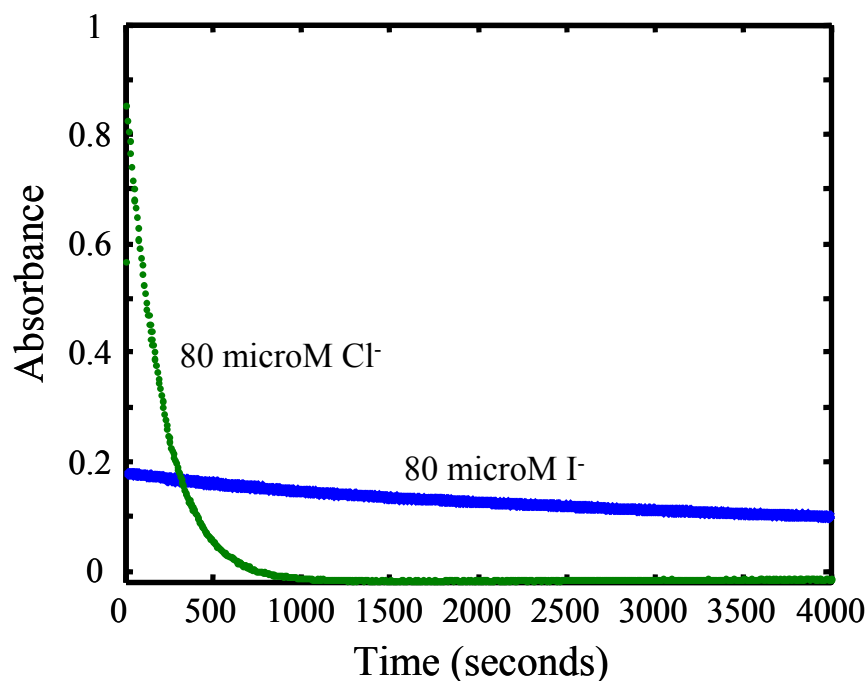


Figure 11. Comparison of Effects of 80 μM Iodide and 80 μM Chloride on Kinetics of Mercuric Ion Reduction

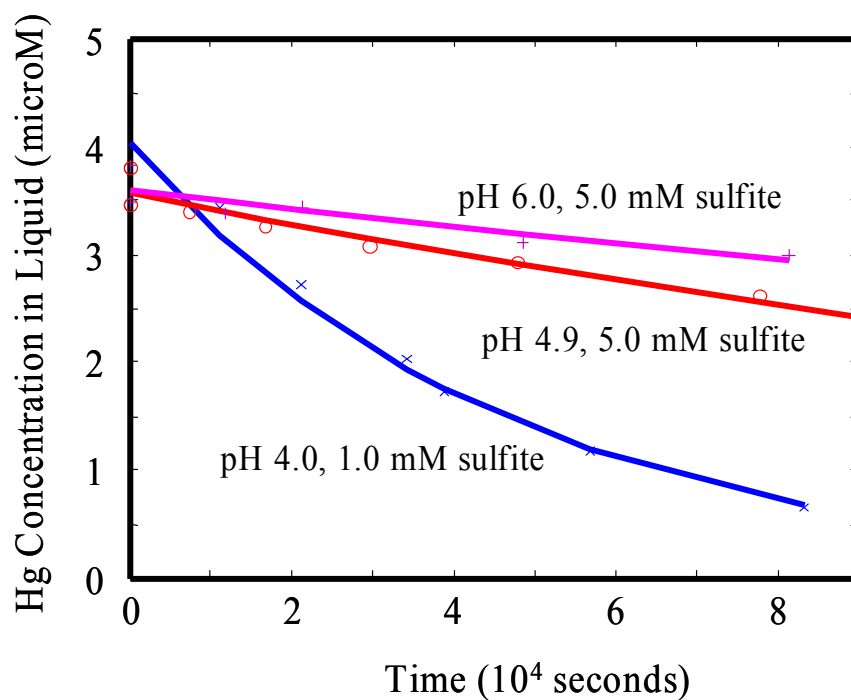


this low concentration. However, iodide, which is known to be a very strong complexing agent for mercuric ion, reduces the rate of reaction substantially. The k_{obs} for the run with 0.080 mM iodide is $1.3 \times 10^{-4} \text{ sec}^{-1}$, similar to but still somewhat slower than that obtained for the 10 mM chloride runs.

In another series of longer-term tests under slow reaction conditions, the Hg^0 stripping apparatus was operated in combination with periodic liquor sampling and cold vapor atomic absorption measurement of oxidized mercury remaining in the liquid phase. Thus, the rate of Hg^0 evolution has been determined for these slower reaction rate conditions by determining the rate at which Hg concentrations drop in the reaction liquor. These runs employed 100 mM acetate buffer to obtain better pH stability for the long run times. This set of runs was done to determine the effect of varying pH (4.0, 5.0, and 6.0) and sulfite concentration (1, 5, and 20 mM) at a fixed chloride value (100 mM) typical of FGD conditions, over a duration of 24 hours.

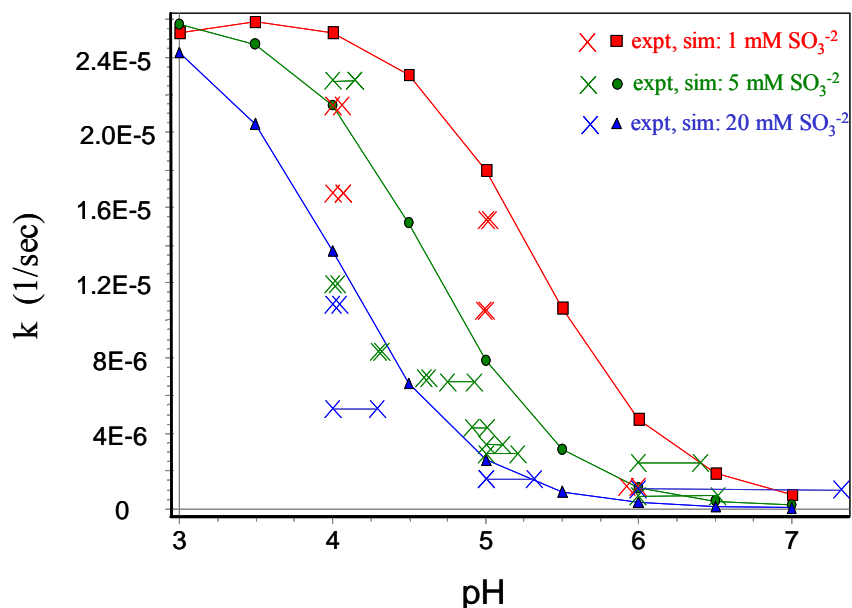
Some examples of individual run results obtained using this method are shown in Figure 12. All runs reported below were done using 100 mM sodium chloride and 100 mM sodium acetate at 55 °C. The inlet SO_2 concentration in the gas mixture was varied from approximately 1 ppm to 200 ppm to match the calculated equilibrium total sulfite value for the desired pH and sulfite concentration.

Figure 12. Amount of Mercury Remaining in Solutions of Compositions Shown, also Containing 100 mM NaCl and 100 mM Acetate Buffer, on Continuous Stripping with $\text{N}_2\text{-SO}_2$ Gas Mixture (Solution spiked with $4.0\ \mu\text{M}\ \text{Hg}(\text{ClO}_4)_2$ at $t = 0$)



Apparent first order rate constants, k_{obs} , were calculated for each run from the first order rate fits. Results obtained thus far are shown in Figure 13. Since there was some variation in pH during the high pH runs in particular, results are plotted for both the initial pH and final pH, joined by a horizontal line for clarity as needed. The lines and solid markers show results obtained from the kinetics model, basing the corresponding k 's on the rate of formation of Hg^0 predicted by the model.

Figure 13. Observed and Model-Simulated Rate Constants for Reduction and Evolution of Mercury in 1.0, 5.0, and 20 mM Sodium Sulfite Solutions as a Function of pH. (Solutions contained 100 mM NaCl and 100 mM sodium acetate at 55 °C).



These results show that the rate of reduction of oxidized mercury increases significantly (by a factor of about 10) as the pH decreases from about 5 to 6 down to pH 4 in the presence of 100 mM chloride. This is consistent with the results obtained at low chloride values using the spectrophotometric method. Although there is considerable scatter, the shape of the rate constant versus pH curve appears to depend on the sulfite concentration. In general, the rate decreases with increasing sulfite concentration, though the dependence seems to be more pronounced in the transition region between high and low pH. The behavior shown here could be particularly relevant to actual FGD systems since it would indicate that the fastest elemental mercury formation rates would occur in the absorber and could even vary with type of absorber, position in the absorber, or FGD chemistry.

As an example, in limestone reagent spray-tower absorbers, the absorber recycle slurry is fed to the spray nozzles at a pH value of about 5.5. As slurry droplets fall through the absorber, countercurrent to the flue gas flow, the droplets are exposed to inlet flue gas with a high inlet SO_2 concentration, and the droplet pH decreases significantly. Values of pH 3 or less are possible. However, in absorbers that operate with high liquid phase alkalinity, such as with magnesium-enhanced lime reagent or with dibasic acid additives, the pH drop can be much less significant. Similarly, absorber types other than open spray towers may have significantly different droplet pH profiles.

KINETICS MODEL RESULTS

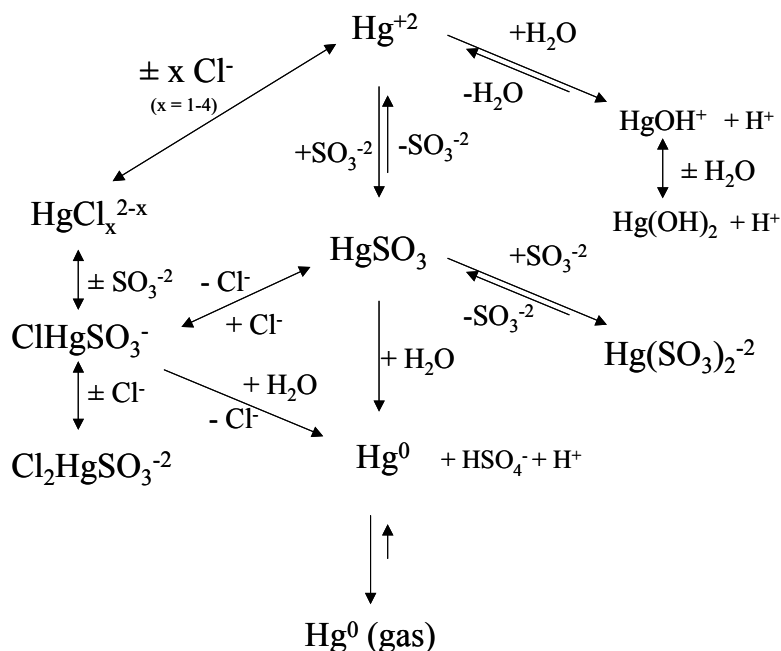
As is the case for most "real world" reacting chemical systems, the reactions under investigation represent composites of several simpler reactions, and are not subject to analytic, single-reaction kinetic equation analysis. Therefore results are being incorporated into a chemical kinetics model

that can numerically solve relatively large systems of chemical kinetics differential equations (representing on the order of 30 to 50 individual reactions). URS Corporation has developed kinetics modeling software that keeps a database of reactions and rate constants along with a database of reaction conditions such as initial concentrations and temperature. A driver program sends these inputs to a very efficient differential equation solver that produces a set of time-dependent concentrations for all species. Experimental data can be easily displayed alongside the calculated results.

This solver simultaneously solves the set of ordinary differential equations using a semi-implicit Runge-Kutta method with automatic interval-step-size adjustment. Given a set of reactions, the rate constants for the reactions, and the initial concentrations of reactants, the program produces concentration-time profiles for all chemical species in the reaction set. The model is developed by entering known or measured rate constants, then fine tuned by comparing experimental time-concentration profiles to the calculated profile and varying unknown or uncertain rate constants until a satisfactory match is obtained over a wide range of conditions of pH, temperature, and ionic strength.

Considerable progress has been made on adapting this general model to the present mercury re-emissions investigation. All of the pertinent reactions found in the Hg-sulfite kinetics literature have been added to the model. In addition, reactions which model mercuric ion-chloride equilibria have been added, although rate constants for most of these reactions are not available and estimates are currently being used. Many of the temperature dependences of the individual rate constants are also unknown. However, relationships between the forward and back rate constants and the heats of reaction were used to obtain an internally consistent data set that allows the proper temperature dependence of the equilibrium constants to be maintained. A simplified schematic depiction of the current model reactions is shown in Figure 14.

Figure 14. Schematic Diagram of Main Reaction Pathways in Current Kinetics Model



In most respects the kinetics model now adequately describes both the short term spectrophotometric results and the long term total mercury stripping results. The model implies that the mechanism of reduction proceeds primarily via the chloromercuric sulfite complexes in more acidic solutions. The chloride essentially provides a ceiling to limit the rate of reaction at low pH. The mechanism changes to primarily occur through the mercuric disulfite complex at higher pH. This change of mechanism could explain some of the "complex" behavior often observed in re-emission results. Even at higher pH the chloromercuric sulfite complexes play a role, because without them the mercuric chloride complexes tend to shut down mercuric reduction completely at approximately the 100 mM (~3500 ppm) chloride level. As shown in Figure 13, the model is predicting the basic trends seen experimentally for pH and sulfite effects, and is giving fairly good numerical agreement with these and the chloride-dependence data.

CONCLUSIONS

Experimental methods have been developed to use spectrophotometry to identify key reaction intermediate species and to track their changes in concentration as the reactions proceed to reduce mercuric species to elemental mercury. Separate but complementary methods of following the rate of evolution of mercury in the gas phase, and loss of mercury from the liquid phase have also been developed and applied. Using these methods, both the rate of disappearance of the mercuric sulfite and chlorosulfite complexes and the rate of formation of elemental mercury product can be monitored by independent means. This work is determining the effects of temperature, ionic strength, initial reactant concentrations, pH, chloride, thiosulfate, and other complexing agents on the rates of these reactions, and thus on the re-emission of Hg from FGD systems.

We have shown that even fairly low concentrations of chloride have a significant effect on the rate of mercuric ion reduction by sulfite. Evidence has been found for the formation of complexes of mercuric ion with both sulfite and up to two chloride ions. Each chloride ion attached to the mercury slows the decomposition of the mercuric chloride complex to elemental mercury by a very substantial amount. The key role played by the sulfite aqueous species (SO_3^{-2}) indicates that other solution components (such as magnesium and calcium) which ion pair with sulfite could also influence the kinetics of mercury reduction. Work is under way to define the potential effects of FGD cations.

Measurements of the rate of stripping of elemental mercury from solution as a function of time have been used to verify and extend the spectrophotometric results to high chloride and long reaction time conditions. In the absence of chloride, the Hg^0 stripping rate measurements confirm the first order disappearance of Hg^{+2} and equivalent rate constants are obtained for this case as well as at low chloride concentrations. At elevated chloride levels the Hg^0 stripping rate measurements show a sharp initial release of elemental mercury, but then very low rates of release are observed for extended times. These results have been verified by measurement of mercury retained in the liquor after each run and expanded by periodic liquid sampling.

The elemental mercury stripping apparatus results show that the rate of reduction of oxidized mercury increases by a factor of about 10 as the pH decreases from 5 to 6 down to pH 4, in the

presence of 100 mM chloride. In general, the rate decreases with increasing sulfite concentration, though the dependence seems to be more pronounced in the transition region between high and low pH. These results suggest that mercury re-emissions in full-scale wet FGD systems could be greatly influenced by factors such as slurry droplet pH drop, sulfite pick up, and sulfite oxidation within the absorber rather than reaction tank conditions.

A chemical kinetics model has been developed to describe the aqueous mercury-sulfite-chloride-thiosulfate system and takes into account the simultaneous occurrence of a number of reaction steps. The model is predicting the basic trends seen experimentally for pH, sulfite, and chloride effects, and is giving fairly good numerical agreement with experimental data. It is being used to design bench-scale experiments for testing as well as to predict kinetics in low pH regions, such as at the SO₂ gas-aqueous interface, which are difficult to investigate experimentally.

Efforts have begun to conduct bench-scale wet FGD tests to validate model predictions. An initial test matrix has been developed, required modifications to the bench-scale FGD apparatus are currently underway, and bench-scale testing will commence soon.

ACKNOWLEDGEMENTS

This work was supported by DOE - NETL, Sara Pletcher, Project Manager, and by the Electric Power Research Institute (EPRI), Richard Rhudy, Project Manager.

REFERENCES

1. Gary M. Blythe and David W. DeBerry, PhD. "Bench-scale Kinetics Study of Mercury Reactions in FGD Liquors, Semiannual Technical Progress Report, October 1, 2004 – March 31, 2005," DOE/NETL Cooperative Agreement No: DE-FC26-04NT42314, April 2005.
2. Gary M. Blythe and David W. DeBerry, Ph.D. "Bench-scale Kinetics Study of Mercury Reactions in FGD Liquors, Semiannual Technical Progress Report, April 1, 2005 – September 30, 2005," DOE/NETL Cooperative Agreement No: DE-FC26-04NT42314, October 2005.
3. Gary M. Blythe and David W. DeBerry, Ph.D. "Bench-scale Kinetics Study of Mercury Reactions in FGD Liquors, Semiannual Technical Progress Report, October 1, 2005 – March 31, 2006," DOE/NETL Cooperative Agreement No: DE-FC26-04NT42314, April 2006.
4. Van Loon, L. L.; Mader, E. A.; Scott, S. L., "Sulfite Stabilization and Reduction of the Aqueous Mercuric Ion: Kinetic Determination of Sequential Formation Constants," *J. Phys. Chem. A*, 105(13); 3190-3195 (2001).

5. Dasgupta, P. K., and K. B. DeCesare, "Stability of Sulfur Dioxide in Formaldehyde Absorber and its Anomalous Behavior in Tetrachloromercurate(II)," *Atmospheric Environment*, 16 (12), 2927, 1982
6. Oda, C. E. and J. D. Ingle, Jr., "Continuous Flow Cold Vapor Atomic Absorption Determination of Mercury," *Anal. Chem.*, 53, 2030 (1981).

DISCLAIMER

This paper was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.